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STRUCTURAL, OPTICAL, AND PHYSICAL PROPERTIES OF GeO2-PbOBi2O3 GLASS

HAMID-REZA BAHARI POOR FARKOOSH

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STRUCTURAL, OPTICAL, AND PHYSICAL PROPERTIES OF GeO_2-PbO-Bi_2O_3 GLASS

By

HAMID-REZA BAHARI POOR FARKOOSH

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of the Requirements for the Degree of Doctor of Philosophy
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DEDICATION

Any beauty, harmony, and knowledge includes in this dissertation has been donated to me from GOD and I pass to him with pleasure. This dissertation dedicated to the only reality of universe, my merciful GOD.

It is dedicated to all merciful humans who tried honestly, bravely and persistently to develop people's realization of universe and help them to leave with happiness, felicity and blessing.

I dedicate this thesis to my family who helped me during my study life. This dissertation is dedicated to my Father who spiritually and financially supported me in all of my study duration, especially in my PhD that which I was fully supported by him. It is dedicated to my Mother because of her continues and deep spiritual supports and encouragements. I dedicate also, this dissertation to my kind Sister who patiently tolerated me and compassionately encouraged me during my stay in Malaysia especially in onerous difficulties.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

STRUCTURAL, OPTICAL, AND PHYSICAL PROPERTIES GeO_2-PbO-Bi_2O_3 GLASS

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December 2012

Chair: Prof Sidek Abd. Aziz, PhD

Faculty: Faculty of Science

The lead bismuth germanate glasses are of growing interest, due to their low cut-off optical phonon energy, high linear and nonlinear refractive index and excellent infrared transmission. Fabrication of metallic nanostructures embedded in glass matrix also attracts many researchers because of their enhancement ability of photoluminescence and optical nonlinearity. However, fabrication of metallic nanostructure other than sphere in glass matrix still is a challenge where met with a very limited success. To achieve the research objectives, the undoped and Er^{3+}/Yb^{3+} doped germanate based glasses samples were prepared. This thesis reports the preparation of GeO_2-PbO-Bi_2O_3 ternary glass system with and without Er^{3+}/Yb^{3+} by melt cast-quenching method. All samples are studied by a wide range of characterization techniques which includes their structure, elastic and optical properties. An attempt has been made to add silver nanostructures into the germanate based glasses by thermal reduction of melt-quenched glass in order to study the formation of nanostructures in the vitreous network.

In the germanate based glasses system the bismuth atom will be substituted by the lead atom to achieve almost mass independent properties due to their closeness of atomic masses. Structure and physical properties were studied by X-ray diffraction, Fourier transform infra-red (FTIR), density, ultrasonic velocities, UV-Visible absorption, photoluminescence and transmission electron microscopy (TEM). All of the samples were fully amorphous and their density, ultrasonic velocities and elastic moduli are relatively low for high lead content samples. FTIR peaks related to PbO covalent bond and bending Bi-O bond of BiO_6 group which are formed when both Pb and Bi act the role of former in glass network, were observed in high lead content samples in contrast with low lead samples. The FTIR data also showed that germanium participated in glass structure with both of four-fold and six-fold coordination in all of samples. The UV-visible absorption of the glasses studied showed highest energy of band-gap for Pb-rich samples and also showed characteristic peaks of Er^{3+}/Yb^{3+} ions. The photoluminescence spectrum obtained by excitation at wavelengths of highest absorption peaks, showed highest intensities for samples with highest lead content which related to lowest non-radiative relaxation in Pb-rich samples.

The GeO_2-PbO glass dopped with Er_2O_3, Yb_2O_3 and $AgNO_3$ were also prepared by melt quenching method. Annealing of the glass were utilized for thermally reducing of Ag^+ ions to metallic silver. The TEM results showed that the annealing process at 450˚C caused the formation of silver nanoparticles of about 3 nm mean diameter size. The samples which were annealed at 400˚C temperature showed the formation of silver nanoplates with mean length size of 60 nm embedded in glass matrix. The

UV-Visible absorption also confirmed the existence of metallic silver nanostructure. The FTIR shows peaks at 470 cm^{-1} for 450˚C annealed samples, in contrast with 400˚C annealed samples, which suggest the existence of Pb-O chains in the germanate glass network. This is the main source of difference in formation of various nano structures due to different stabilizing medium and better physical isolation of glass matrix in 450˚C annealed samples.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falasafah

STRUKTUR, SIFAT-SIFAT OPTIK DAN FIZIKAL KACA GeO_2-PbO-Bi_2O_3

Oleh

HAMID-REZA BAHARI POOR FARKOOSH

Disember 2012

Pengerusi: Prof Sidek Abd. Aziz, PhD

Fakulti: Fakulti Sains

Kaca bismut germanat semakin diminati penyelidik disebabkan oleh tenaga optik fonon bertenaga rendah, indeks pembiasan linear dan tak linear yang tinggi serta proses penghantaran inframerah yang baik. Fabrikasi nanostruktur logam yang berada dalam matrik kaca juga menarik perhatian ramai penyelidik kerana keupayaannya dalam peningkatan fotoluminesen dan juga ketaklinearan optik. Walau bagaimanapun, fabrikasi nanostruktur logam selain daripada sfera di kaca matrik masih merupakan satu cabaran dengan sedikit kejayaan. Bagi mencapai objektif kajian, kaca germanat yang didop dantanpa didop dengan Er^{3+}/Yb^{3+} telah berjaya disediakan. Tesis ini melaporkan penyediaan sistem kaca ternari GeO_2-PbO-Bi_2O_3 yang didop dan tanpa dengan Er^{3+}/Yb^{3+} menerusi kaedah acuan leburan pelindapan. Kesemua sampel dikaji menerusi pelbagai teknik pencirian termasuklah struktur, sifat elastik dan optik. Satu usaha telah dilakukan dengan menambah nanostruktur

perak ke dalam kaca berasaskan germanat menerusi kaedah pengurangan terma peleburan bagi mengkaji pembentukan nanostruktur dalam rangkaian kaca.

Bagi semua kaca germanat, atom bismut akan digantikan dengan atom plumbum untuk mencapai kebebasan dari faktor jisim disebabkan jisim atom mereka yang hampir sama. Struktur dan sifat fizikal dikaji menerusi pembelauan sinar-X, jelmaan Fourier infra-merah (FTIR), ketumpatan, halaju ultrasonik, penyerapan UV-nyata, fotoluminesen dan juga mikroskop elektron transmisi (TEM). Semua sampel sepenuhnya amorfus dan ketumpatan, halaju ultrasonik dan modulus elastik adalah agak rendah bagi sampel kaca berkandungan plumbum yang tinggi. Puncak FTIR yang berkaitan dengan ikatan kovalen PbO dan ikatan kelenturan Bi-O bagi kumpulan BiO_6 terbentuk apabila kedua-dua Pb dan Bi berperanan sebagai pembentuk rangkaian kaca; perkara ini telah diperhatikan bagi sampel berkandungan plumbum yang tinggi berbanding dengan sampel berkandungan plumbum yang rendah. Data FTIR juga menunjukkan bahawa germanium mengambil peranan dalam struktur kaca dengan kedua-dua koordinasi iaitu empat dan enam –lipatan dalam kesemua sampel. Penyerapan UV-nyata bagi kaca kajian menunjukkan jurang tenaga tinggi bagi sampel yang kaya Pb dan juga menunjukkan puncak ciri bagi Er^{3+}/Yb^{3+} ion. Spektrum fotoluminesen diperolehi menerusi pengujaan pada jarak gelombang puncak penyerapan, menunjukkan keamatan tertinggi bagi sampel dengan berkandungan plumbum yang tinggi dan berkaitan dengan proses relaksasi terendah bukan radiatif bagi sampel tersebut.

Kaca GeO_2-PbO didop dengan Er_2O_3, Yb_2O_3 dan $AgNO_3$ juga disediakan menerusi kaedah leburan pelendapan. Proses penyepuhlindapan kaca telah dilaksanakan bagi menukar ion Ag^+ kepada logam perak. Hasil kajian TEM menunjukkan bahawa proses penyepuhlindapan pada 450˚C berupaya membentuk nanopartikel perak bergarispusat purata kira-kira 3 *nm*. Sampel yang telah disepuhlindap pada suhu 400˚C menunjukkan pembentukan nanoplat perak bersaiz purata 60 *nm* panjang tertanam dalam matrik kaca. Penyerapan UV nyata juga mengesahkan kewujudan nanostruktur logam perak. Data FTIR menunjukkan puncak 470 cm^{-1} pada 450˚C bagi sampel tersepuhlindap, berbanding pada suhu 400˚C ; hal ini mengesahkan kewujudan rantaian rangkaian Pb-O kaca germanat. Ini adalah sumber utama perbezaan dalam pembentukan pelbagai struktur nano kerana kelainan kestabilan media dan pengasingan fizikal matrik kaca pada 450˚C bagi sampel yang disepuhlindap.

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This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Sidek Haji Abd Aziz, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Chairman)

Halimah Mohamed Kamari, PhD
Senior Lecturer
Faculty of Science
Universiti Putra Malaysia
(Member)

Wan Mahmood Wan Yunus, PhD
Professor
Faculty of Science
Universiti Putra Malaysia
(Member)

Faisal Rafiq Bin Mohamd Adikan, PhD
Senior Lecturer
Faculty of Engineering
University of Malaya
(Member)

____

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has notbeen previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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Hamid-Reza Bahari Poor Farkoosh

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